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Medium Range Interactions Evidences in Compounds with Aliphatic Lateral Chain : 1-Pentanoic Acid, 1-Pentanol and Pentylammonium Nitrate as Test Cases

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Abstract

In this study we have explored by means of polarizable molecular dynamics simulations and small-angle X-ray diffraction, a subset of liquids belonging to the following three different classes of compounds: pentyl ammonium nitrate, 1-pentanol and 1-pentanoic acid. The presence of a low-Q peak in the X-Ray spectra of the liquids provides evidence that a long alkyl chain is connected to the polar moiety and it is sufficient to establish nanodomain segregation in the liquid. From the calculations, we have obtained the theoretical scattering patterns that reproduce very nicely the experimental spectra in the low-Q ranges. From detailed analyses of the radial distribution functions, we infer that the medium-range ordering in these liquids stems from the joined effects of both strong and weak interactions.

Keywords: SAXS, RDFs, Pre-Peak, I(Q), Polarizable

1. Introduction

Room Temperature Ionic Liquids (RTILs) represent an especially intriguing class of compounds since they show a series of remarkable properties that

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make them appealing for both academic and applicative issues.(1; 2; 3; 4; 5) Among their properties, their well-known low vapor pressure(6) and high thermal and chemical stability,(7) make them optimal substitutes for typically polluting volatile organic solvents (VOC). Furthermore a new generation of low toxic ionic liquids for human and plants has been recently synthesized.(8; 9; 10; 11; 12) From the structural point of view, one of the main studied subset is represented by protic ionic liquids (PILs). They are synthesized by combining Brønsted acids and bases.(13; 14; 15; 16; 17; 18; 19; 20; 21) In detail, PILs, whose most typical feature is the presence of a cation having a polar group and an aliphatic lateral chain, exhibit the presence of a strong hydrogen bond network and a very interesting feature observed in the X-Ray diffraction pattern, the evident low-Q diffraction peak (sometimes called pre-peak).(22; 23; 24) This behavior holds when the chain is at least three carbon atoms long (25; 23) and reflects the establishment of structural periodicities in bulk RTILs that stem from nanoscopic interactions between their molecular constituents and include both long-range Coulombic forces and short-range van der Waals ones.(26; 25; 27) Under this scenario, in a recent work,(28) Pethes *et al.* have shown that the pre-peak is detected even in the experimental X-ray diffraction pattern of neat liquid 1-pentanol. As this class of compounds consists of a polar moiety (the hydroxyl group) and an aliphatic chain as well, it would seem that the pre-peak is observed whenever the two structural motifs are present. Yet, the same authors show that the prepeak unexpectedly is almost totally lacking for aldehyde 1-pentanal. In order to shed more light on this issue, we have decided to use a technique capable of yielding good structural insight, as Small Angle X-Ray Spectroscopy (SAXS) on three different compounds, namely pentylammonium nitrate (PeAN), 1-pentanol (PenOH) and 1-pentanoic acid (PenCOOH). The sketch of the molecules is reported in Fig.(1).

We have chosen these systems as object of our study because they belong to three different class of compounds (PILs, alcohol and carboxylic acid) but they are characterized by the same structural motifs: one polar group and an aliphatic chain. The experimental data were interpreted with the aid of molecular dynamics (MD). Due to strong anisotropic H-bond interactions, standard two-body force fields fail in describing polarization and many body effects in ILs in a reliable way;(29) for this reason, further improvement is needed in the theoretical treatment, as for instance tuning the point charges.(24; 30) Furthermore, all-atom type force fields (31; 32) fail in reproducing low-Q peaks for n-pentanol compounds.(28) Within these premises,

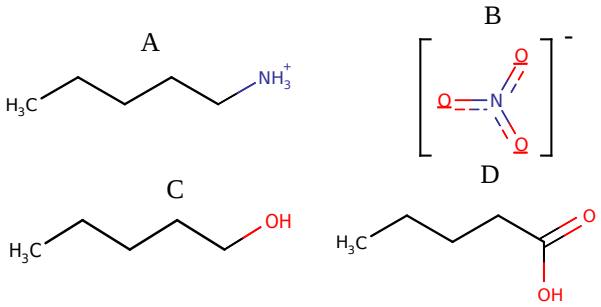

Figure 1: Sketch of the studied systems : (A) pentylammonium, (B) nitrate, (C) 1-pentanol and (D) 1-pentanoic acid.

we have exploited the atomic multipole optimized energetics for biomolecular applications (AMOEBA)(33) force field to perform MD. It explicitly includes charge polarization through the induced multipoles experienced by each atom, due to the electric field originated by the surrounding charge distribution. One has to remind that the approach has proved effective for many liquid systems.(34; 35; 23)

1.1. Experimental Details

The PIL was synthesized according to the procedure already described in (27), while the other two systems were purchased from Aldrich. Small angle diffraction experiments (SAXS) were collected on a Bruker AXS D8 Advance focusing powder diffractometer operating in transmission mode in θ/θ geometry, equipped with a Cu-Kα X-Ray tube ($\lambda = 1.5407$ Å). Capillaries were fixed, upside down, using bee-wax, to a standard goniometer head and aligned along the beam path. The instrument is fitted with focusing Göbel mirrors along the incident beam, Soller slits on both incident (2.3° horizontal divergence) and diffracted (radial) beams, and a Vantec-1 position sensitive detector (PSD). Data were measured in step-scan mode in the 240° 2θ angular range, step-size 0.022° 2θ and 1s counting time. After the data treatment, the structure function I(Q) was obtained, which is sensitive to the pairwise distances between the atoms of the system:

$$I(Q) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j f_i f_j \times \left[4\pi\rho_0 \int_0^{\infty} r^2 (g_{ij}(r) - 1)\frac{sinQr}{Qr} dr\right]. \qquad (1)$$

In the formulae above, x_i are the numerical concentrations of the species, f_i their Q-dependent X-ray scattering factors, N is the number of the different atomic species and ρ_0 is the bulk number density of the system. This methodology has been successfully applied to the study of molecular(36) and ionic liquids,(19; 37; 26) as well as solutions.(38)

1.2. Computational Details

To investigate the structure of the pure liquids we considered three different simulation boxes, composed of 300 ion pairs for PeAN and 400 molecules both for PenOH and PenCOOH. For all the systems, a pre-equilibration was performed with classical molecular dynamics within periodic boundary conditions, using the AMBER(39) program-package and the Gaff(40; 41) force field. A 5-ns-long equilibration trajectory was produced for the systems in the *NPT* ensemble; the simulation temperature was set at 298 K. The difference between MD and experimental density was less than 5%. The edges (L) of the cubic cells are: 41.94 Å (PeAN), 41.66 Å (PenOH) and 41.78 Å (PenCOOH). The box dimensions were chosen by considering that a box edge at least equal to twice the correlation length is needed to reproduce the low-Q peak of the structure factors, and to ensure good statistics (see the Results for more details). The respective densities (ρ) are: 1.03 g/cm^3 (PeAN), 0.82 g/cm^3 (PenOH) and 0.95 g/cm^3 (PenCOOH). Only for PeAN, the point charges has been scaled of 0.8 factor to mimic polarization effects between the cations and the anions.(42) The final configurations of each fixed-charge classical trajectory were used as starting points for the polarizable molecular dynamics simulations. They consist in 2 ns productive dynamics in the *NVT ensemble*. The beeman integrator and Halgren buffered 7-14 form for the van der Waals interactions were used, while the time step was set to 1 fs. The calculations were run with the program AMBER, using the MPI parallel version of pmemd.amoeba.(39) The system topologies were prepared according to the Poltype(43) procedure developed by AMOEBA authors, which includes the calculation of intramolecular parameters and of static multipoles (up to quadrupole) through GDMA (distributed multipole analysis) of wave functions calculated using the Gaussian program(44)). The full Amber topologies are available upon request, due to the large file dimensions.

2. Results

The corrected and normalized experimental total scattering structure factors from SAXS experiments are shown in Fig.(2), together with their weighted counterparts calculated from polarizable molecular dynamics simulation results. All the three compounds qualitatively show the same characteristic features: (a) presence of a pre-peak located at Q values lesser then 1 $Å^{-1}$ (falling at 0.38 $Å^{-1}$, 0.54 $Å^{-1}$ and 0.46 $Å^{-1}$, going from PeAN to PenCOOH passing through the PenOH) (b) presence of a principal peak located at 1.59 $Å^{-1}$ for PeAN, 1.45 $Å^{-1}$ for PenOH and 1.44 $Å^{-1}$ for PenCOOH. These findings comply with the peaks reported by Greaves *et al.*(45; 46) and Pethes *et al.*(28) for PeAN and PenOH respectively. As already discussed in the literature (22; 10; 9) the pre-peak can be attributed to the existence of a medium-range order brought about by the segregation of alkyl portions among the polar moiety of the bulk liquid. The second feature can be mostly ascribed to spatial correlations occurring in the distance range 3-5 Å, which for these liquids might have intramolecular origin (head-to-tail contacts) as well as might be due to intermolecular hydrogen-bond interactions. Considering the comparison between simulated and theoretical patterns, we can see that the location of the two peaks is well reproduced by our theoretical model for all the three liquids. The emulation of the relative intensities unfortunately fails for PeAN and PenCOOH. For the former molecule, the force field tends to overestimate the principal peak, whereas for the latter one the pre-peak is boosted. Regarding PenOH, the experimental SAXS pattern is perfectly reproduced by the theoretical one. We can state that, on average, the main features of the experimental data are covered by our theoretical approach. The total scattering pattern can be divided into the individual contributions coming from each pair of scatterers (see Eq. 1) which can be, in turn, clustered into group terms. For the sake of determining the most important contributions to the pre-peak, we extracted the partial structure factors of the following atom clusters: anion and cation for PeAN, hydroxyl group and aliphatic chain for PenOH and carboxyl group and aliphatic chain for PenCOOH. The results are reported in Fig.(2). As one can see from Fig.(2), anion-anion interactions have the largest contribution to the PeAN pre-peak. In a similar way, the medium-range order, in the other two liquids, is originated exclusively from interactions involving the hydroxyl-hydroxyl and the carboxyl-carboxyl contacts. This result is compliant with the hypothesis of hydrophobic contacts between alkyl chains that induce a separation between

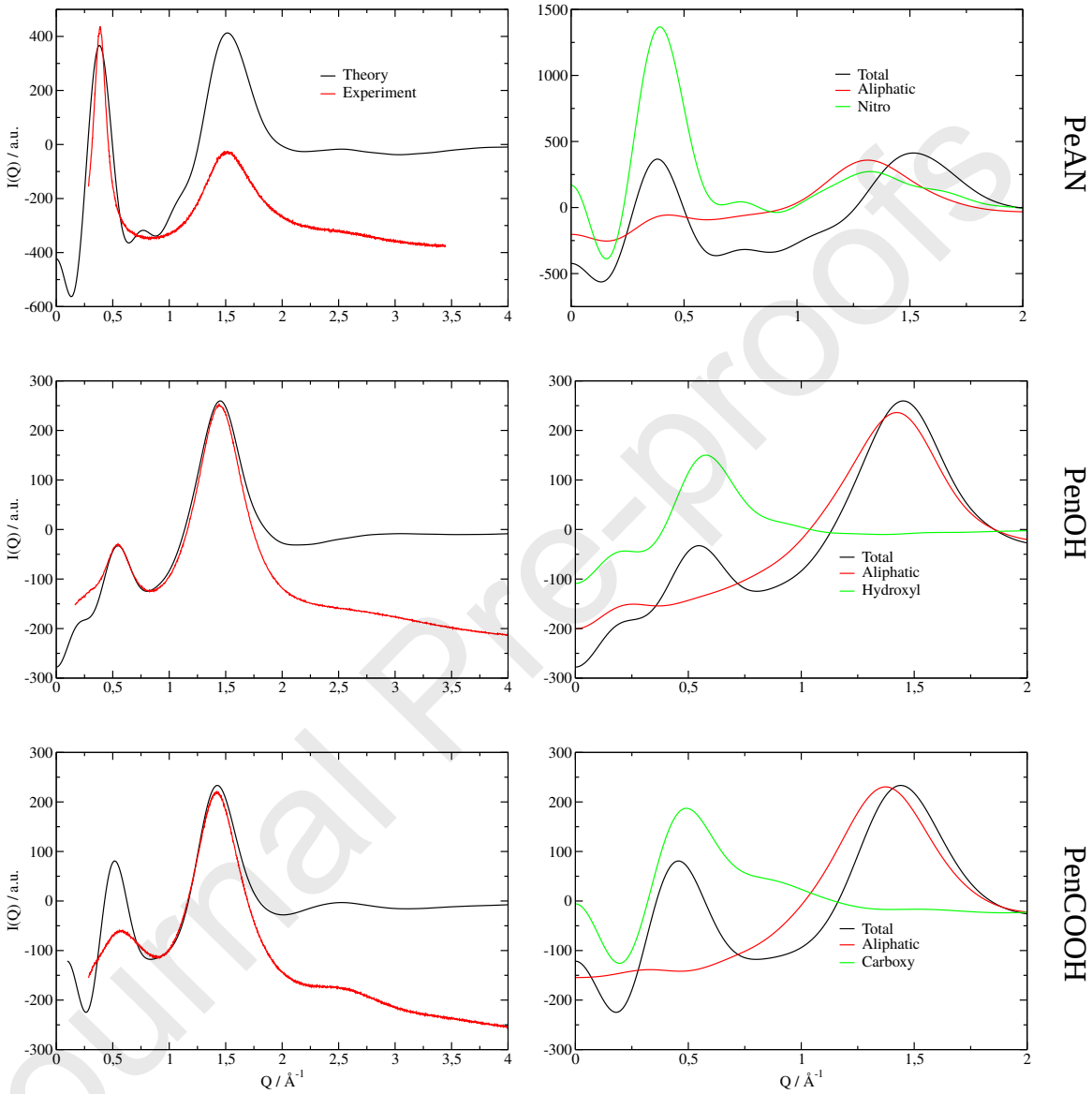

Figure 2: Left Panels: experimental *vs.* theoretical SAXS diffraction patterns. Right Panels: total and partial theoretical SAXS.

second neighbor polar groups. The quality of the agreement with the experimental data makes us confident that our calculations are representative of

the system, and could be used for further analysis of the microscopic structure of the liquids. For this purpose we have analyzed some of the partial radial distribution functions (RDFs) that have been calculated directly from the simulated atomic coordinates. We focus on the RDFs that reveal the two most important interactions of these compounds, namely the H-bonds and weak interactions between alkyl chains. The H-bond interaction is characterized by the N(Cat)$\cdots$O(Ani) contacts for PeAN and O-H$\cdots$O contacts for the others, while the weak interactions by the distance between the terminal carbon atoms of the aliphatic chain. These RDFs are collected in Fig. (3). By looking at PeAN, the present MD simulation clearly points out the first

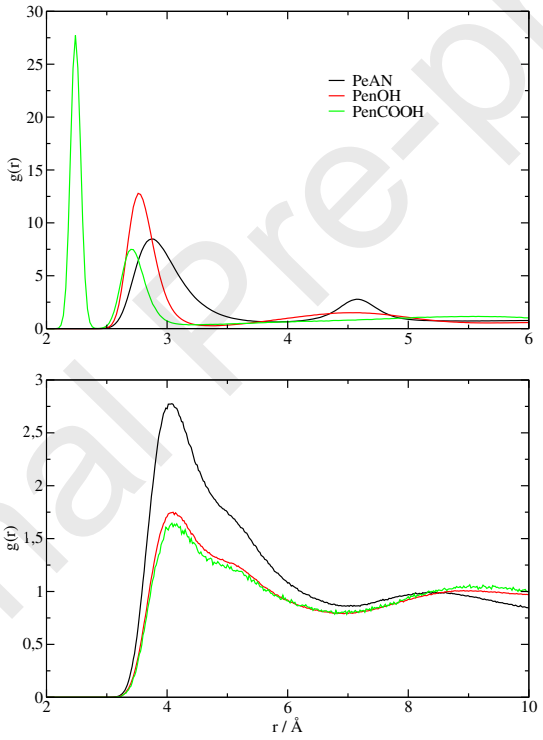

Figure 3: Upper panel: RDF of N$\cdots$O distance (PeAN) and O-H$\cdots$O (PenOH and PenCOOH). Lower Panel: correlations involving the terminal carbon atoms of the alkyl chains.

shell N$\cdots$O distance around 2.85 Å, a value which agrees with some of the previous data.(47; 48; 27) The structure beyond the main peak that consists

of one small peak around 4.7 Å is due to the tridentate nature of the anion acting as hydrogen bonds acceptor. Regarding PenOH, as expected, we find only one peak falling at about 2.77 Å due to the contacts between hetero atoms. PenCOOH shows two separated peaks at 2.24 Å and 2.71 Å instead. The former comes from an intramolecular interaction between the oxygen atoms beloging to the carboxyl group, while the latter from intermolecular H-bonds. Because of its greater electronegativity, the carboxyl group is a stronger H-bond donor/acceptor then the hydroxyl one, hence it shows a shorter O-H$\cdots$O equilibrium distance. By looking at the bottom panel of Fig. (3) we see that the alkyl chains originate a weak correlation, centered at about 4.2 Å. In this case apart from the relative intesities, all the liquids exhibits the same equilibrium value.

3. Conclusions

For the first time in this work, a common feature in compounds characterized by a polar and an aliphatic chain has been shown. For our scope we have reported a comparison between experimental small X-ray scattering profiles and MD simulations for three different liquids: pentyl ammonium nitrate, 1-pentanol and 1-pentanoic acid. These systems belong to three different class (ILs, alcohol and carboxyl acids), however they can be outlined by the same semplified representation: one polar moiety (ammonium group plus nitrate anion for PeAN, hydroxyl group per PenOH and carboxyl group for PenCOOH) connected to an aliphatic later chain. The agreement between experiment and model is very good and enables to trace reliable and relevant structural information about liquid phase. These kind of liquids, are organized in a partially ordered three-dimensional network that experience, locally, an alternation between polar and apolar moieties. Such alternation patter give rise to a peak in the X-ray diffraction pattern, located at low Q value below 1 Å^{-1}. That event comes out from the interplay between the strong H-bond interactions, which tend to make the system rigid, and the hydrophobic interactions, due to the alkyl chains, which induce aggregation phenomena that locally weaken the cohesive energy.

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Highlights:

•SAXS patterns of three different compounds are reported for the first time.

•The patterns show the presence of prepeaks in these kinds of systems.

•Experimental data are successfully reproduced with polarizable molecular dynamics.

•Thanks to the theoretical data it was possible to dissect the different contributions to the total SAXS patterns.

Declaration of interests

■ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: